

II.B.5 High Pressure Distributed Ethanol Reforming

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direction determined annually by DOE

- Down-select separation technology for distributed bio-derived renewable liquid feedstocks reforming. (4Q, 2010)
 - The pressurized reforming pathway offers the advantage of a larger driving force in separation processes that rely on partial pressure gradients. The project will further evaluate other separation and purification membrane options.
- Demonstrate pilot-scale use of integrated separation (membrane) reactor system for renewable feedstocks. (1Q, 2012)
 - If the initial results from the pressurized reforming in a membrane reactor appear sufficiently promising, the concept may be demonstrated at the pilot scale in collaboration with industrial partners.

Objectives

- Evaluate the high-pressure steam reforming of ethanol as an option for the distributed production of hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Fuel Processor Capital Costs
- (E) Greenhouse Gas Emissions
- (H) System Efficiency

Contribution to Achievement of DOE Distributed Reforming Milestones

This project will address the following DOE Hydrogen Production milestones from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Down-select research for distributed production from distributed renewable liquids. (4Q, 2010)
 - This project is evaluating the technical feasibility of reforming ethanol, a renewable bio-derived liquid, at an elevated pressure to save on downstream hydrogen compression costs for a distributed hydrogen production facility.

Accomplishments

- Designed and fabricated a membrane reactor and apparatus to study the effectiveness of hydrogen extraction on the kinetics and hydrogen yield during the steam reforming of ethanol at an elevated pressure.
- Measured the hydrogen transported across the membrane to establish the hydrogen flux as a function of temperature and pressure differential. The results were fitted to models to obtain the activation energies. The analysis indicated a change in transport mechanism at ~300°C.
- Initiated catalytic reaction studies and mathematical modeling of the reactor that is being set up to extract global kinetic parameters.



Introduction

Distributed hydrogen production facilities will need to store and transport hydrogen at pressures in excess of 5,000 psig. This is typically achieved by compressing the product hydrogen, where the compression (from 150 psig) consumes ~18% of the lower heating value of the hydrogen produced, a significant parasitic load on the overall process efficiency. In this project, we are investigating the option of steam reforming ethanol at elevated pressures, since this pathway can eliminate or greatly reduce the energy cost of compression by feeding a pressurized liquid stream into the reformer.

The challenges in high-pressure reforming of ethanol include: (1) high hydrocarbon and low hydrogen yields (at a given temperature and steam-to-carbon ratio)

avored at thermodynamic equilibrium; (2) an increased tendency to form coke deposits; and (3) the potentially higher capital cost associated with pressurized equipment. On the other hand, the high-pressure process offers the advantages of a more compact system (greater reactivity) and higher driving force for pressure-based separation/purification systems. The system design needs to balance these diverse characteristics to meet an efficiency target (for calendar year 2012) of 72%, to produce hydrogen at a cost of \$3.80 per gallon of gasoline equivalent.

Approach

An experimental apparatus has been set up to study the ethanol steam reforming reaction as a function of the catalyst formulation, space velocity, steam-to-carbon ratio, temperature, and pressure. The catalytic reactor has been redesigned to include a hydrogen transport membrane for the removal of hydrogen from the reaction zone to promote the kinetics and shift the equilibrium towards higher hydrogen yields. The hydrogen permeation can be stopped by shutting off a valve on the permeate side, thereby enabling an evaluation of the yields with and without hydrogen separation within the reactor. A model of the micro-reactor is being developed, which will be used to determine the kinetics of hydrogen transport and the reforming reaction, and to identify the mechanisms that limit the reaction rate, conversion, and product selectivity. The experiments will be conducted at reaction temperatures and pressures up to 800°C and 1,000 psig, respectively.

Results

The experimental reactor was redesigned to incorporate a hydrogen transport (Pd-alloy) membrane. The 3.2-mm (1/8-in) outside diameter, 25.4-mm (1-in) long membrane tube was purchased from REB Research and Consulting. The apparatus has been modified to enable measurement of the amount of hydrogen permeating across the membrane. Initial tests have been conducted to measure the hydrogen flow across the membrane and to calculate the flux as a function of the reactor temperature and pressure. For these measurements, the permeate side was maintained at 1-atm pressure. Figure 1 plots the hydrogen permeation rate as a function of temperature and pressure; as expected, the permeation rate increases with temperature and pressure. The hydrogen flux (J) was calculated from the permeation rate. The maximum hydrogen permeation rate for this membrane, with its 30- μm -thick Pd-alloy film on a 43- μm -thick support layer, was measured at 32 ml/min (at 1 atm, 25°C), which corresponds to a calculated flux of 12.7 ml/cm²-min, at 650°C and 300 psig feed pressure. The

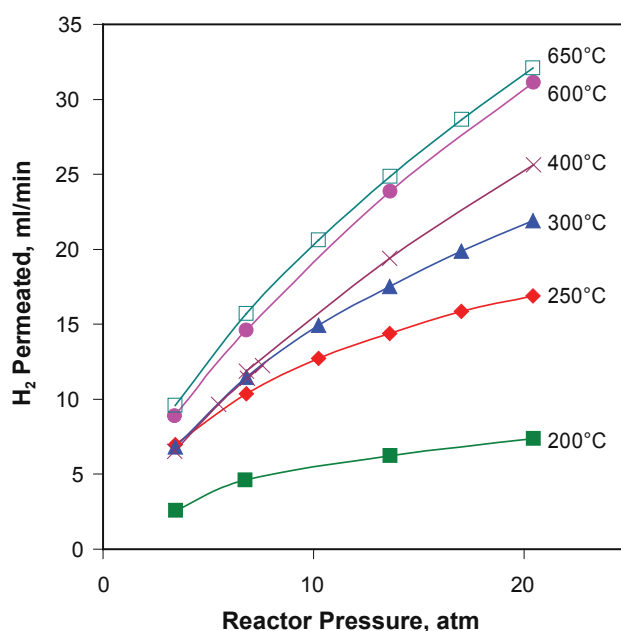


FIGURE 1. Hydrogen permeated across a Pd-alloy membrane tube as a function of the upstream pressure. Permeate side pressure was maintained at 1 atm.

permeation tests were limited to 300 psig because the maximum hydrogen partial pressure in the catalyst zone is expected to be less than 300 psig, when the reaction is conducted at 1,000 psig. The highest flux achievable in these tests is lower than DOE's target value of 101 ml/cm²-min at a pressure difference of 20 psig across the membrane.

The hydrogen flux was fitted to an equation of the form of Sievert's law,

$$J = k [(P_{\text{H}_2,\text{hi}})^{1/2} - (P_{\text{H}_2,\text{lo}})^{1/2}], \quad \text{where } k = A_0 e^{(-E/RT)}$$

to determine an apparent activation energy (E) for the rate of hydrogen transport through the Pd membrane. Figure 2 shows the flux of hydrogen plotted as a function of the partial pressure driving force. Figure 3 is used to extract the apparent activation energy and shows that the data are best fitted with two straight lines. Below 300°C, the activation energy is 24.8 kJ/mol; above 300°C, the calculated apparent activation energy is 4.7 kJ/mol, which is somewhat lower than that reported in the literature [1]. It has been reported [2] that above 300°C, the surface sorption and dissociation of the hydrogen molecule are fast and the rate is controlled by the diffusion of the hydrogen atoms through the metal. In this temperature region, the hydrogen transport follows Sievert's law. At lower temperatures, the sorption and dissociation steps control the hydrogen transport, which is then not predictable per Sievert's equation.

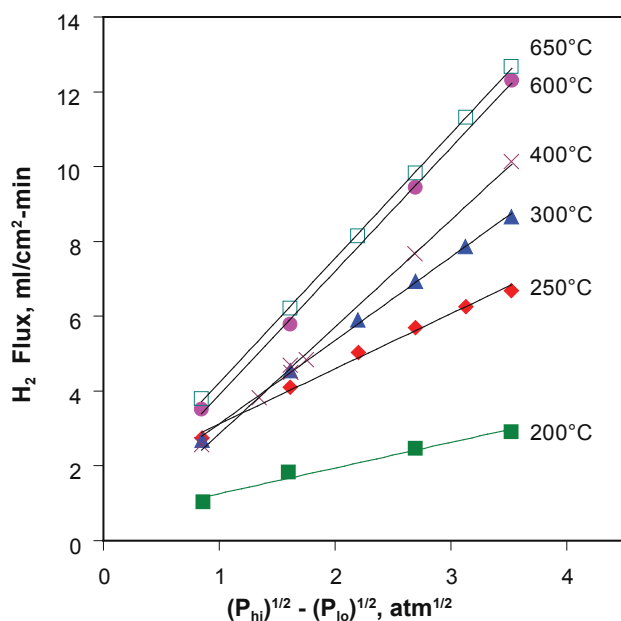


FIGURE 2. Hydrogen Flux across the Membrane as a Function of the Driving Force, to Determine the Value of Sievert's Constant (k)

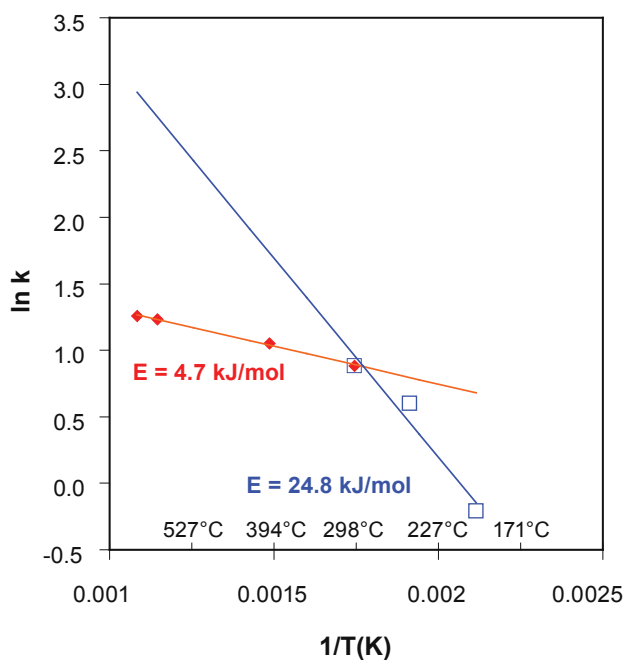


FIGURE 3. Estimation of the Activation Energy (E) using the Arrhenius Equation

A model of the membrane reactor is being developed to extract the global kinetics and to delineate the controlling mechanisms. The model was exercised to evaluate the effect of hydrogen permeation, obtained from the permeation experiments discussed above, when the reforming kinetics are very fast. The use of fast kinetics is reflected in the curves for the hydrogen

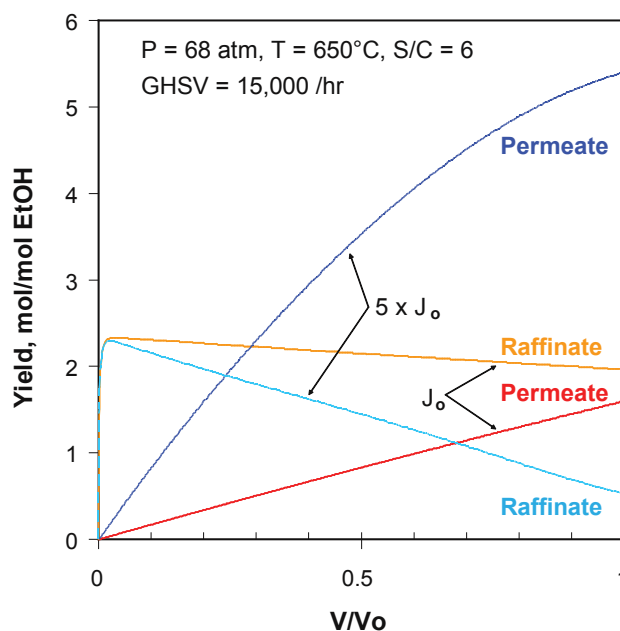
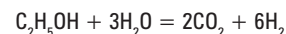


FIGURE 4. Simulation results showing the hydrogen yield that may be expected assuming fast reforming kinetics. J_o represents the flux based on the experimental data in Figures 1-3. The curves for $5 \times J_o$ show the effects of achieving higher permeation rates.

yields in the raffinate streams (see Figure 4), where the hydrogen yield rises to ~ 2.5 mols/(mol of ethanol) very near the reactor inlet. The rest of the reactor essentially serves to permeate the hydrogen, which in turn leads to additional hydrogen production via methane reforming and water-gas shift reactions. For the permeation rates corresponding to current data (J_o) and under the conditions specified, 1.6 mols of hydrogen permeate across while ~ 2 mols leave with the reformate in the raffinate stream. If the permeation rate can be increased by a factor of five, then that case is represented by the curves indicated by ($5 \times J_o$). That scenario would lead to the recovery of 5.5 mols of high purity hydrogen, from a theoretical maximum achievable of 6 mols per mol of ethanol, according to the reaction:



Conclusions and Future Directions

- A membrane reactor and a mathematical model for it have been set up to evaluate the effect of hydrogen removal on the pressurized steam reforming of ethanol.
- The hydrogen permeation rate has been measured as a function of temperature and pressure.
- The hydrogen permeation rate with current membrane dimensions is an order of magnitude lower than the DOE target. The use of thinner

membranes to increase the rate can significantly improve the hydrogen yield.

- The reaction kinetics and achievable hydrogen fluxes will be used to assess, from a fuel processing system perspective, the prospects for continuing R&D on a hydrogen-permeation membrane-reactor.

FY 2007 Publications/Presentations

1. S.H.D. Lee, S. Ahmed, R.K. Ahluwalia, "Steam reforming of ethanol at elevated pressure for hydrogen production," poster presentation at the 2006 Fuel Cell Seminar, Honolulu, HI, November 13-17, 2006.

References

1. Basile, A., Gallucci, F., Paturzo, L., "A dense Pd/Ag membrane reactor for methanol steam reforming: Experimental study," *Catalysis Today*, **104**, pp. 244-250, 2005.
2. Baker, R.W, *Membrane Technology and Applications*, McGraw Hill, 2000.